

COMPRESSIBILITY FACTOR OF NATURAL GASES
AT 60°F AND ONE ATMOSPHERE

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INTRODUCTION

Modern analytical techniques have markedly improved the accuracy with which the composition of a gas can be measured. For many years fuel gases were analyzed by volumetric techniques, such as the Orsat or Podbielniak. Heating values and specific gravities were also determined at atmospheric conditions for pure components and fuel gas mixtures, thus resulting in real gas values. However, because of low accuracy in the analytical methods, particularly with respect to determination of the heavier hydrocarbons, differences between calculated and observed heating values were generally ascribed to experimental techniques, and not interpreted on the basis of gas law deviations.

With the advent of the mass spectrometer, more accurate and complete analyses of gas mixtures may be obtained. These analyses are on a true mole fraction, or ideal gas, basis. Also, accurate ideal gas heat of combustion values can now be derived from the work of Rossini et al., API Project 44⁹. However, full utilization of this improved accuracy can not presently be obtained in the calculation of real gas heating values and specific gravities. The lack of sufficient data to permit accurate prediction of the compressibility factor for real gas mixtures may result in significant differences between measured values and those calculated from the gas analysis. Largest deviations occur in fuel gases containing appreciable quantities of heavier constituents.

An experimental program was therefore planned to obtain compressibility factor data at 60°F and one atmosphere on fuel gas components and mixtures. It was anticipated that these data would provide the basis for development of generalized procedures for prediction of compressibility factors of gas mixtures. This project was undertaken as part of the continuing basic research program of the Institute of Gas Technology, and was sponsored by The Peoples Natural Gas Company. The results obtained for natural gas components and mixtures are reported here.

Methods used for determination of gas compressibility factor fall into two groups: 1) gas density, and 2) pressure-relative volume measurement. In the first group of methods, gas density is measured by gas balance or by direct weighing in a bulb. The compressibility factor is calculated from the expression:

$$z = \frac{pV}{RT} \quad (1)$$

where V is the volume of one mole calculated from the density and molecular weight of the gas. The accuracy of this method depends on absolute values of pressure, volume and temperature.

In the second group of methods, measurements of pressure and relative volume are made over a range of pressure, and pV or a related parameter is extrapolated to zero pressure, as in the Burnett method.² A method of this kind for use at pressures near atmospheric was described by Jessen and Lightfoot.⁶ Data are obtained at two or three different pressures by confining the sample of gas in progressively larger volumes over mercury. The compressibility factor is calculated by fitting the pV measurements (V is the measured volume here) with an equation such as:

$$pV = (pV)_0 \quad z = (pV)_0 (1 + \beta p) \quad (2)$$

Here the accuracy depends primarily on relative volume and pressure measurements, and constancy of temperature, rather than on absolute values of these quantities. Absolute values of pressure and temperature affect the result in a much less critical way; that is, by the dependence of z on pressure and temperature, and not by the dependence of pV and RT . Similarly the accuracy of z for mixtures is not affected by the dependence of gas density on composition. However, the method is dependent on the linearity of z with pressure.

According to the statistical mechanical expressions for virial coefficients in the equation

$$pV = RT (1 + Bp + Cp^2 + \dots) \quad (3)$$

the second virial coefficient, B , represents the deviation from ideal behavior involving collisions between two molecules.⁵ From this theory it also follows that the second virial coefficient for mixtures involves only binary interaction terms, and is of the form:

$$B_m = x_1^2 B_1 + x_2^2 B_2 + x_3^2 B_3 + \dots \\ + 2x_1 x_2 B_{12} + 2x_1 x_3 B_{13} + 2x_2 x_3 B_{23} + \dots \quad (4)$$

where B_1, B_2, B_3, \dots are second virial coefficients of the pure components, and $B_{12}, B_{13}, B_{23}, \dots$ are interaction coefficients. The latter can be evaluated by experimental determination of B_m 's on binary mixtures, together with knowledge of the B 's for pure components. The effect of the third virial coefficient at one atmosphere is very small and is considered later.

Five components usually occur in natural gases in concentrations of 5% or more: methane, ethane, propane, carbon dioxide and nitrogen. Minor amounts of isobutane, *n*-butane, isopentane and *n*-pentane also occur, together with traces of heavier hydrocarbons. A review of the literature indicated that sufficiently reliable values of atmospheric pressure compressibility factors are available for the major components,^{1,4} but not for the minor components. Also, although only very limited data were available on mixtures of these components, the data indicated that composition had a very sizeable effect on compressibility factor.

Therefore, compressibility factor measurements were made on the pure butanes and pentanes, and on a series of selected mixtures. The interaction coefficients among the five major components, and of methane with the four minor components, were determined. In addition, the interaction coefficients of n-butane with all major components was measured to provide a basis for prediction of those not determined experimentally.

APPARATUS

The apparatus is shown in Fig. 1. The mixture preparation system, gas expansion system, mercury reservoir and the lower part of the mercury manometer are mounted in a water bath with a plate-glass front. The temperature of the bath was maintained within 0.05° of 15.55°C (60°F), and did not vary more than 0.01°C during any one run.

A and B are Hoke stainless steel cam-closing valves. Connection to glass parts is made through stainless steel Swagelok fittings and 1/8-in. stainless steel tubing sealed to the glass with Dekhotinsky cement. Other valves are Hoke toggle or needle valves. The upper part of the long manometer arm extends out of the bath and is equipped with a jacket for water circulation. Manometer arms and jacket are constructed of precision bore tubing; arms 1 and 2, 12 mm ID; arm 3, 13.8 mm ID. Vacuum is maintained at 0.02 mm or less with a mechanical vacuum pump and dry ice cold trap, and is read with a tilting McLeod gage sensitive to 0.01 mm Hg. Mercury levels are read to 0.05 mm with a Gaertner 100 cm cathetometer.

The mixture preparation bulbs, gas expansion bulbs, and manometer arm 1 were calibrated by weight of mercury delivered. The volume of valve B and the capillary manifold in the expansion system, and the volume between valves A and B and the top of the upper bulb in the mixture preparation system, were determined with a 10 cc gas burette. The volume between the top and bottom menisci of the manometer arm 1, and corrections for capillary depression, were taken from Kistemaker^{7,8}.

MATERIALS

The hydrocarbons used were Phillips research grade. According to the supplier, purity of the methane was 99.68 mole %, with impurities of ethane and nitrogen. Purity of the other hydrocarbons was 99.9% or better. The carbon dioxide was Matheson, bone dry grade; the nitrogen was Matheson prepurified. Components other than nitrogen and methane were condensed in the freezeout trap to remove air. The part of the apparatus being filled was flushed with the component before filling.

PROCEDURE

In making binary mixtures the first component was measured in the gas expansion system. The second component was measured in the mixture preparation system by means of manometer arms 2 and 3. Then valve A was closed and the gases were mixed by being forced from one buret to the other several times. A similar procedure was followed in making multicomponent mixtures, except that the intermediate components were measured one at a time in the mixture preparation buret and transferred to the gas expansion buret. Gas

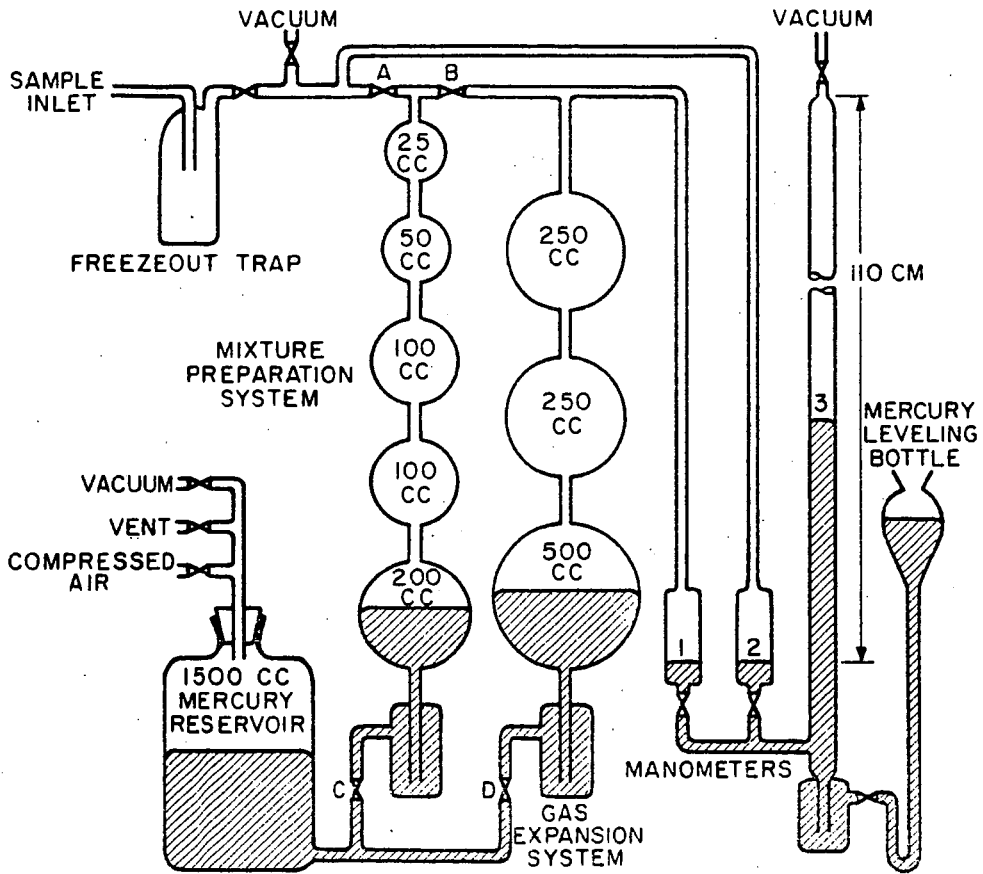


Fig.1.-SCHEMATIC DIAGRAM OF LOW PRESSURE P-V APPARATUS WITH INTEGRAL VOLUMETRIC MIXTURE PREPARATION SYSTEM

remaining in the section between valves A and B after the transfer was discarded.

In most cases, the two upper bulbs of the gas expansion buret were filled to a pressure of about 950 mm Hg. Three to five readings of the top and bottom of the mercury menisci in the two arms of the manometer, and of a reference point on manometer arm 1 were taken. The position of the mercury was changed a millimeter or so for each reading, to minimize the effect of local imperfections of the manometer tubing and plate glass window. Similar readings were taken after the gas was expanded to fill all three bulbs. Measurements on C_5 hydrocarbons had to be taken at lower pressures; a maximum of about 80% of saturation pressure was used.

The apparatus was constructed with three bulbs to allow measurements at three different pressures on the same charge of gas in order to detect variation of the slope β in equation (2) with pressure. However, from variances of the pV measurements at different pressures, it was concluded that better accuracy might be obtained if only the larger volumes were used since volume measurement as well as pressure measurement contributed to the error. Accordingly, data at lower pressures was obtained by removal of part of the sample and repeating measurements on the same two combinations of bulbs.

Data were fitted to equation (2) by least squares computation on an Alvac III digital computer.

COMPRESSIBILITY FACTORS OF PURE COMPONENTS

Results for the coefficient β equation (2) obtained on C_4 and C_5 paraffin hydrocarbons are presented in Table 1. Determinations at lower pressures were made as a part of Runs 2 and 6 on n -butane, and of Runs 3 and 4 on isobutane, to detect the change of coefficient with pressure. A trend in the direction of smaller numerical values of the coefficient at lower pressures is evident. Such tests were confined to the C_4 hydrocarbons, since the effect is barely detectable with them and is likely to be less with lighter hydrocarbons and with mixtures. Determination on the C_5 hydrocarbons at necessarily lower pressures would not yield significant results on this question.

In order to obtain the best value of $1-z$ (1 atm, 60°F), the third virial coefficient was introduced to account for the observed trend of β with pressure:

$$\frac{pV}{(pV)_0} = z = 1 + Bp + Cp^2 \quad (5)$$

An approximation formula was derived from which values of B and C/B could be evaluated from two measured values of β and the average initial and final pressures, p_1 and p_2 of each run

$$B = \beta \left[1 - \frac{C}{\beta} (p_1 + p_2) \right] \quad (6)$$

The ratio C/B was evaluated by application of formula (6) to the data from pairs of runs on the same sample, one made at normal pressures

Table 1. GAS LAW DEVIATIONS OF C₄ AND C₅ PARAFFIN HYDROCARBONS
AT 60° F.

Run No.	β (atm ⁻¹)	$p_1 + p_2$ (atm)	Atmospheric Gas Law Deviation $b = 1 - 2$
<u>n-Butane</u>			
1	-0.03413	1.901	0.03361
2a	-0.03466	1.826	0.03417
2b	-0.03433	1.437	0.03410
2c	-0.03422	1.044	0.03419
3	-0.03423	1.849	0.03374
4	-0.03453	1.830	0.03404
5	-0.03411	1.846	0.03362
6a	-0.03437	1.862	0.03387
6b	-0.03397	1.458	0.03370
6c	-0.03416	1.027	0.03414
Weighted Avg.			0.03394
			-0.00008 (a)
<u>Isobutane</u>			
1	-0.03022	1.894	0.02982
2	-0.02993	1.891	0.02953
3a	-0.03013	1.889	0.02973
3b	-0.02973	0.937	0.02970
4a	-0.03022	1.881	0.02982
4b	-0.02942	0.895	0.02947
Weighted Avg.			0.02971
			-0.00010 (a)
<u>n-Pentane</u>			
1	-0.05504	0.578	0.05570
2	-0.05632	0.525	0.05703
Weighted Avg.			0.0565
			-0.0007 (b)
<u>Isopentane</u>			
1	-0.05199	0.723	0.05236
2	-0.05076	0.766	0.05107
Weighted Avg.			0.0518
			-0.0005 (b)

(a) From pooled variance of b values for both butanes.

(b) From variance of the pV measurements.

and the other at about half the normal pressures. Runs 2a with 2c, and 6a with 6c, on n-butane, and Runs 3a with 3b, and 4a with 4b, on isobutane, give C/B ratios of 0.016, 0.007, 0.014 and 0.026, respectively. The average of the four, weighted according to the variance of the pV measurements, was 0.016; its standard deviation, also calculated from the variance of the pV measurements, was 0.006.

It was desirable to apply similar corrections to our results for C₃ hydrocarbon and mixtures. However, the C/B ratio for lighter gases at 60°F is smaller than those observed for the butanes, e.g., ethane, 0.006^{1,3}, while higher ratios are theoretically expected for heavier hydrocarbons³. The observed ratio of C/B for the butanes was approximately equal to B/2. In order to correct our results on a consistent basis over the complete range of deviations, we adopted a C/B ratio of B/2 for all the hydrocarbons and mixtures.

Gas law deviations of the C₄ and C₅ hydrocarbons, in the form of 1-z for easy comparison with the uncorrected β values, are shown in Table 1. Maximum error of the compressibility factors of the butanes is estimated to be 0.03%, and for the pentanes, 0.1%.

Values of gas law deviations for pure components used in the calculation of data on mixtures are collected in Table 3.

BINARY INTERACTION COEFFICIENTS

Interaction coefficients determined by measurement of the compressibility factors of binary mixtures of natural gas components are presented in Table 2. These have been calculated by means of the mixture rule of equation (4) but using the gas law deviation (1-z) rather than actual second virial coefficients. Since the third and higher virial coefficients make only a small contribution (maximum about 1%) to the deviation, error from this approximation should not be significant.

Estimated standard deviations of the methane - n-butane and methane - n-pentane averages are 0.00034 and 0.00045, respectively. The estimated standard deviation of other average interaction coefficients is 0.00022.

Agreement of experimental gas law deviations with the mixture rule was tested by determinations of interaction coefficients on 1:3 and 3:1 mixtures of methane with n-butane, and of carbon dioxide with n-butane. On the carbon dioxide - n-butane system, agreement is within experimental error and no trend is apparent. On the methane - n-butane system, a trend of increasing interaction coefficient with increasing methane content is noticeable; however, the difference between 3:1 and 1:3 coefficients is not significant at the 90% confidence level. Compressibility factors of the methane - n-butane mixtures calculated from the average interaction coefficient reported in Table 2 agree with the determined values within 0.06% maximum deviation, and agree to 0.03% on the average.

Table 2.-COMPRESSIBILITY AND INTERACTION COEFFICIENT OF BINARY MIXTURES
OF NATURAL GAS COMPONENTS

Mixture	Composition Mole % First Component	Gas Law Deviation b_m^*	Interaction Coefficient $b_{1,2}^*$	Mixture	Composition Mole % First Component	Gas Law Deviation b_m^*	Interaction Coefficient $b_{1,2}^*$
Methane-Ethane	50.6 50.7	.00472 .00441	.00436 .00376 Avg .00406	Nitrogen-Methane	50.0 50.6	.00091 .00093	.00072 .00078 Avg .00075
Methane-Propane	49.7 50.3	.00798 .00771	.00590 .00558 Avg .00574	Nitrogen-Ethane	50.1 50.3	.00344 .00334	.00254 .00236 Avg .00245
Methane-Isobutane	48.6 49.9	.01155 .01137	.00651 .00688 Avg .00669	Nitrogen-Propane	48.4 48.4 48.4	.00682 .00650 .00682 Avg .00671	- - - - - - - - - Avg .00344
Methane-n-Butane	72.1 74.8 75.1 48.5 48.7 23.6 23.7 24.6	.00702 .00626 .00583 .01326 .01323 .02251 .02190 .02174	.00843 .00806 .00711 .00765 .00773 .00724 .00567 .00634	Nitrogen-n-Butane	49.7 49.8 49.3	.00622 .01039 .01070	.00352 .00382 Avg .00367
Methane-Isopentane	59.8 59.7	.01345 .01358	.00917 .00933 Avg .00925	Carbon dioxide- Methane	49.6 49.5	.00318 .00323	.00260 .00270 Avg .00265
Methane-n-Pentane	59.3 60.5 59.9	.01542 .01479 .01544 Weighted Avg .01132	.01107 .01103 .01180 Avg .01132	Carbon dioxide- Ethane	49.5 49.1	.00630 .00602	.00532 .00494 Avg .00523
Ethane-Propane	50.5 50.2	.01266 .01259	.01222 .01162 Avg .01192	Carbon dioxide- Propane	49.0 50.1	.00977 .00992	.00744 .00800 Avg .00777
Ethane-n-Butane	49.9 49.8	.01830 .01859	.01542 .01592 Avg .01567	Carbon dioxide- n-Butane	74.5 49.5 50.2 24.6	.00924 .01498 .01456 .02322	.00975 .00990 .00942 Avg .00978
Propane-n-Butane	50.4 49.6	.02504 .02499	.02426 .02388 Avg .02407	Carbon dioxide- Nitrogen	49.6 50.0	.00220 .00259	.00144 .00218 Avg .00181

* $b_m = x_1^2 b_{1,1} + 2 x_1 x_2 b_{1,2} + x_2^2 b_{2,2}$ where b_1 , b_2 are gas law deviations (1-2) at one atmosphere for the mixture, pure component 1, and pure component 2, respectively, at mole fractions x_1 and x_2 of the components in the mixture.

COMPLEX MIXTURES

In the Benedict-Webb-Rubin equation the linear square root combination is used to predict constants for mixtures from constants for the pure components for the second virial terms. Applied to our parameter this yields:

$$b_m = \left[\sum_i x_i b_i^{1/2} \right]^2 = \sum_i x_i^2 b_i + 2 \sum_{i \neq j} x_i x_j b_i^{1/2} b_j^{1/2} \quad (7)$$

Comparison with equation 4 indicates that interaction coefficients for a given component i should lie on a straight line of slope $b_i^{1/2}$ if plotted against $b_j^{1/2}$. This plot is shown in Fig. 2. Experimental points fall reasonably close to the predicted value, except for carbon dioxide mixtures. In order to retain the advantages of the linear square root combination for calculating the compressibility factor of complex mixtures, a pseudo b value for carbon dioxide has been calculated (Table 3).

Two four-component mixtures were prepared and their gas law deviations measured to test methods of predicting the compressibility factors of complex mixtures. The measured values are presented in Table 4, together with values calculated by:

- 1) Linear combination of gas law deviations of components,
- 2) Mixture rule with binary interaction coefficients, equation (4), and
- 3) Linear square root combination of gas law deviations of pure components equation (7), with the pseudo deviation for carbon dioxide.

These results indicate that the compressibility factor of complex mixtures can be calculated by either 2) or 3) with an accuracy of 0.05% or better. This represents a distinct improvement over the linear combination.

Heating values of gas mixtures are sometimes calculated by a summing of terms of the form $x_i H_{r,i}$, where $H_{r,i}$ is the real gas heating value of the pure component. This formula yields values for the two mixtures in Table 4 which are about 3 Btu per SCF, or almost 0.3%, too high. As a result of this study it is recommended that the heating value be calculated on the basis of the ideal gas heating values, and be corrected for nonideality by the mixture compressibility factor, calculated by either of the recommended combining rules, methods 2) or 3). By this procedure the error of calculation for the mixtures in Table 4 is reduced to only 0.3 Btu/SCF, or 0.03%.

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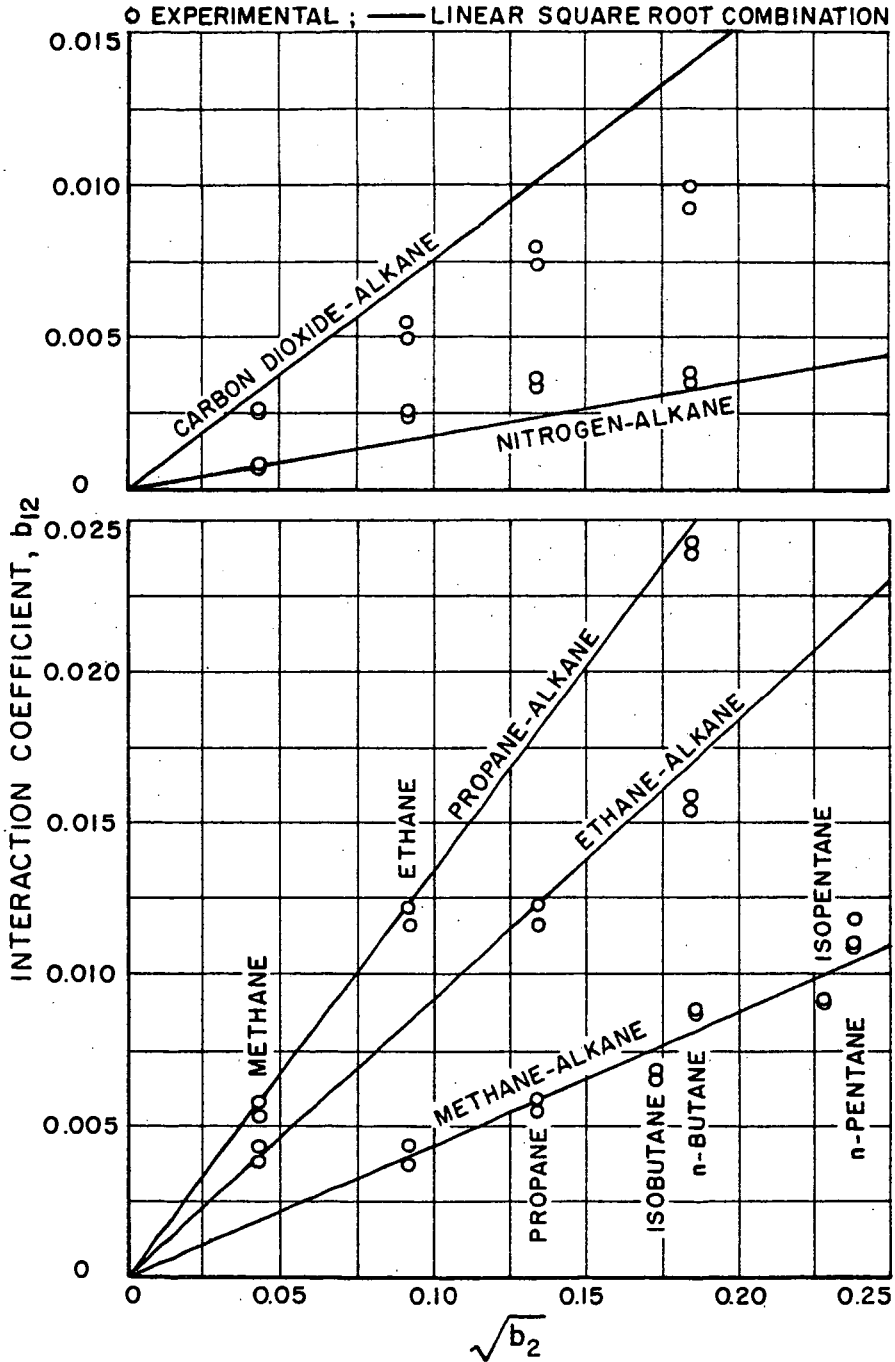


Fig. 2.-COMPARISON OF EXPERIMENTAL AND CALCULATED INTERACTION COEFFICIENTS OF NATURAL GAS COMPONENTS

Table 3. GAS LAW DEVIATIONS OF NATURAL GAS COMPONENTS AT 60°F AND ONE ATMOSPHERE

<u>Hydrocarbon</u>	<u>Gas Law Deviation $b = 1 - z$</u>	<u>Source</u>
Methane	0.0019	API ¹
Ethane	0.0084	API ¹
Propane	0.0180	API ¹
Isobutane	0.0297	IGT
<u>n</u> -Butane	0.0339	IGT
Isopentane	0.0518	IGT
<u>n</u> -Pentane	0.0565	IGT
Nitrogen	0.0003	NBS ⁴
Carbon Dioxide	0.0057*	NBS ⁴

* For calculation by linear square root combination, use the pseudo value, $b = 0.0041$.

Table 4. GAS LAW DEVIATIONS OF FOUR-COMPONENT MIXTURES AT 60°F AND ONE ATMOSPHERE

	<u>Mixture 1</u>	<u>Mixture 2</u>
Methane, mole %	67.44	64.14
Ethane, mole %	16.37	20.68
Propane, mole %	5.30	5.02
Nitrogen, mole %	10.89	0.00
Carbon Dioxide, mole %	0.00	10.16
b_m measured	0.00274	0.00331
b_m calculated* (1)	0.00364	0.00444
(2)	0.00292	0.00357
(3)	0.00285	0.00362

* b_m calculated from (1) $b_m = \sum x_i b_i$
 (2) $b_m = \sum x_i^2 b_i + \sum 2x_i x_j b_{ij}$
 (3) $b_m = (\sum x_i b_i^{1/2})^2$

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